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Chrysocolla Redefined as Spertiniite

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Abstract. XAFS and µ-XAFS spectra were collected at the Cu K-edge for seven chrysocolla samples (Peru, USA, and Congo). The results suggest that that the local structure around Cu is similar to that in $Cu(OH)_2$ (spertiniite). Cu-L_3 STXM imaging and spectroscopy confirm that the chrysocolla samples examined here consist of mesoscopic Cu(II)-rich domains surrounded by Si-rich domains (in agreement with results from infra-red spectroscopy). Hence, we suggest that chrysocolla, which is generally considered to be orthorhombic with composition $(Cu,Al)_2H_2Si_2O_5(OH)_4 \bullet nH_2O$, is in actually a mesoscopic assemblage composed dominantly of spertiniite ($Cu(OH)_2$), water and amorphous silica (SiO_2).

Keywords: copper, chrysocolla, spertiniite, XAFS, XANES, STXM, EXAFS, wavelet, nanomineralogy
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INTRODUCTION

Chrysocolla is a blue mineral of composition ~ $(Cu,Al)_2H_2Si_2O_5(OH)_4 \bullet nH_2O$. Its exact structure is unknown despite reported by some (such as the International Mineralogical Association) to be orthorhombic (but unknown space group). Previously, the local atomic arrangement around Cu in chrysocolla was derived using XAFS spectroscopy from that of dioptase ($CuSiO_2(OH)_2$) [1]. In this study, we re-evaluate this model using 7 representative chrysocolla samples from Peru, USA, and Congo (R.D.). Three spatial scales were investigated, including the macro-scale [using X-ray absorption fine structure (XAFS)], the micro-scale [using µ-XAFS], and the nano-scale [using scanning X-ray transmission microscopy (STXM)].

EXPERIMENTAL

Seven chrysocolla samples were selected from various localities in Peru, the Congo D.R., and the USA. The sample colors ranged from pale- to deep blue, deep green, and brown to nearly white (Table 1). We also studied Cu-containing minerals, particularly blue colored ones, such as azurite, cuprorivaite, turquoise and spertiniite (among eleven others). Macroscopic Cu K-edge XANES and EXAFS spectra were collected (high-resolution, Si(220)) on BL 11-2 at SSRL (Stanford, USA) in the fluorescence mode. Cu K-edge µ-XANES spectra were collected (Si(111)) on BL 10.3.2 at the ALS (Berkeley, USA) with a 5x7 µm spot size. STXM images were collected on branch line 11.0.2.2 at the ALS (Berkeley, USA) at the Cu-$L_{3/2}$ edges). Finely ground powders (in deionized water) were deposited on a Cu-mesh. XAFS spectra were reduced using standard methods ("XAFS" [2] and "WAVELETS" [3] codes).

TABLE 1. Chrysocolla sample list.

Sample	description	observations
Mine Ouest, Mashamba, Shaba, Congo D.R.:		
#1	pale greenish blue	with cuprite
Inspiration mine, Globe-Miami, Arizona, USA :		
#2	sky-blue, UL	Cheah et al. (2000)
Ray mine, Pinal Co, Arizona, USA:		
#3	sky-blue	composite sample,
#4	brownish vein	with three areas of different colors,
#5	white crusts	manually separated
Lily mine, Pisco Umay, Ica, Peru:		
#6	deep blue area	composite, with
#7	deep green area	two areas/colors, manually separated

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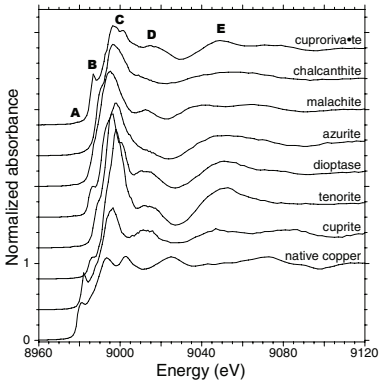

FIGURE 1. Cu K-edge macro-XANES spectra for model compounds of copper. A is the pre-edge feature for Cu(II).

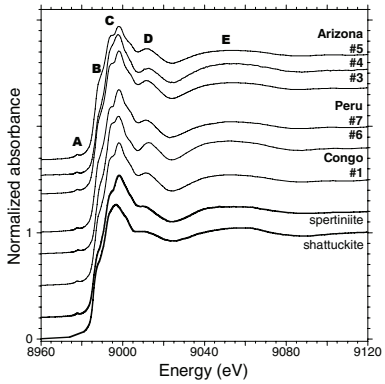

FIGURE 2. Cu K-edge macro-XANES spectra for 5 chrysocollas, as compared to spertiniite and shattuckite.

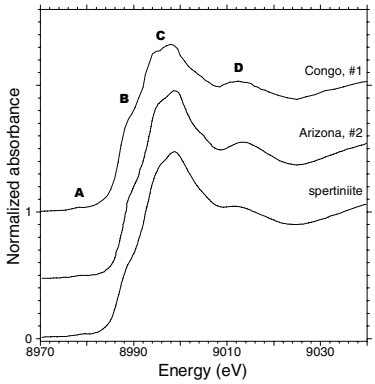

FIGURE 3. Cu K-edge μ-XANES spectra for the Congo #1 and Arizona #2 samples, as compared to spertiniite.

RESULTS

The high-resolution Cu K-edge XANES spectra for all Cu(II)-bearing model compounds show a pre-edge feature (labeled A in Fig. 1) and a shoulder in the edge jump (feature B in Fig. 1). The main edge (feature C) shape varies depending on the model compound (Fig. 1). The high-resolution Cu K-edge macro XANES spectra for the chrysocolla samples are identical (Fig. 2) and are typical of Cu(II) in a distorted Jahn-Teller environment (feature A is detected in all samples). However, the main edge region for the seven chrysocolla samples differs significantly in shape from most other Cu(II)-bearing minerals, except for synthetic spertiniite ($Cu(OH)_2$).

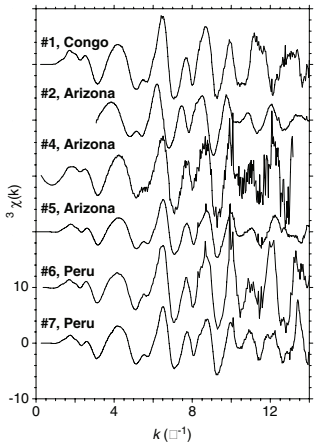

FIGURE 4. Cu K-edge normalized macro-EXAFS (k^3-weighted) for six selected chrysocollas.

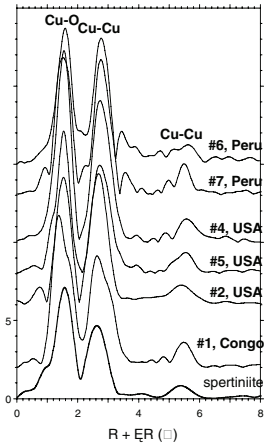

FIGURE 5. Cu K-edge macro-XANES spectra for six selected chrysocolla, as compared to that for spertiniite ($Cu(OH)_2$).

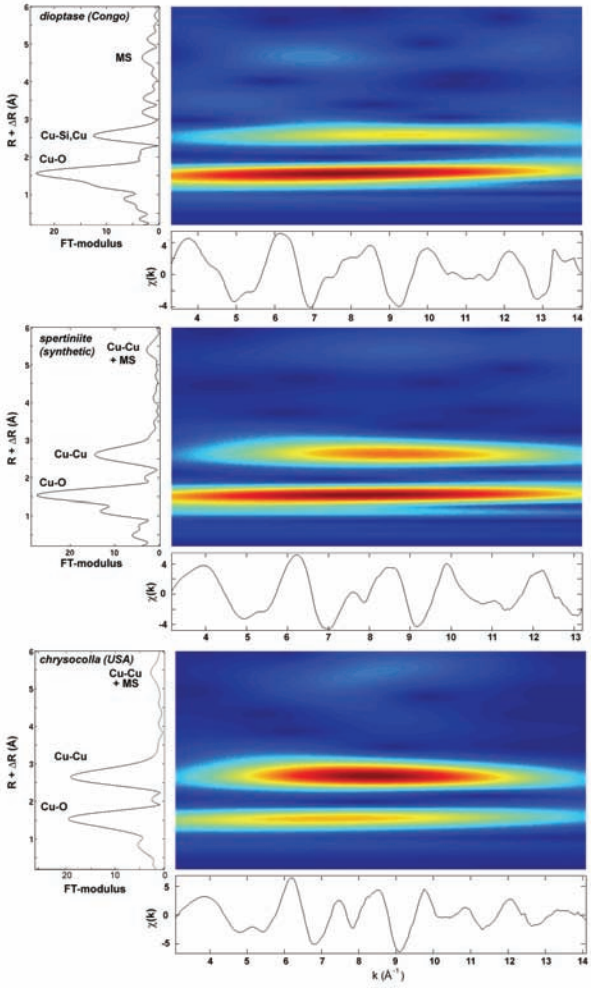

FIGURE 6. Wavelet transforms of the Cu K-edge normalized-, k^3-weighted EXAFS spectra for dioptase (top), spertiniite (middle), and chrysocolla #2 (bottom)(see [4] for details).

The Cu K-edge µ-XANES spectra collected for two samples from the Congo (#1) and Arizona (#2) (Fig. 3) are also very similar to these obtained for spertiniite ($Cu(OH)_2$). The distribution of Cu in these samples is relatively homogeneous at this multi-micron scale. In addition, EXAFS spectra for all chrysocolla samples studied are remarkably similar (Fig. 4). In the Fourier transforms (FT; Fig. 5), the main peak arises from oxygen first neighbors, centered near 2.3 Å (backscattering phase-shift corrected using "XAFS"). The medium-range environment around Cu in the seven chrysocolla samples is characterized by two main pair correlations, centered near 4 and 5.5 Å (not corrected for backscattering phase-shifts).

Then, wavelet transforms (WT) of the k^3-weighted normalized EXAFS spectrum for one chrysocolla sample (#2) is compared to those computed for dioptase and spertiniite (Fig. 6). There are similarities in the WT's among these two models and chrysocolla, including a region near k ~ 7-9 $Å^{-1}$(R+ΔR ~ 5.5 Å), which is clearly related to Cu next-nearest neighbors.

Finally, STXM images (collected over the energy range 930-950 eV at the Cu $L_{3/2}$ edges; Fig. 7) show highly contrasted domains 50-100 nm in size, which are enriched in divalent copper (Fig. 7c). Around these copper-rich domains, the less contrasted domains are depleted in copper. They have to be enriched in silicon in order to account for the sample stoichiometries.

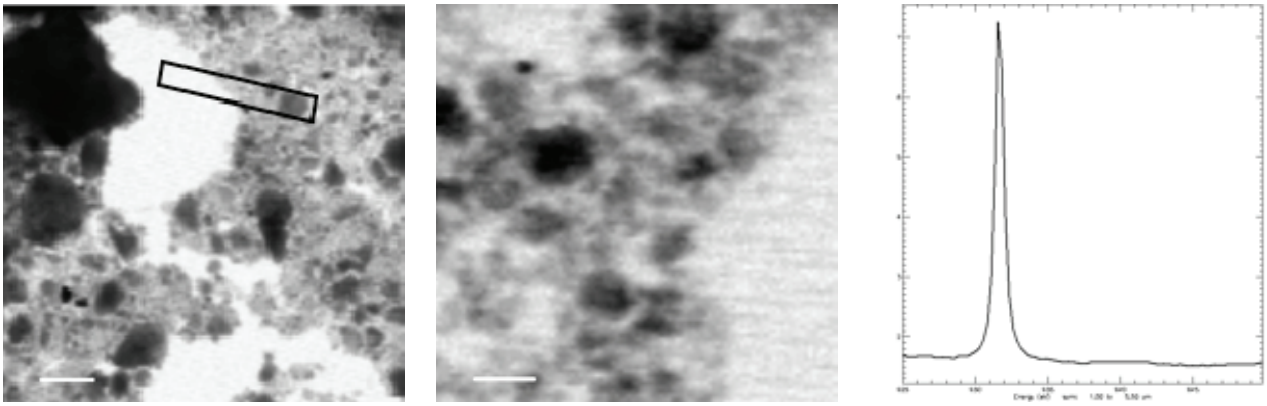

FIGURE 7. STXM images (at 930 eV) for two chrysocollas (left: #1, Congo; middle; #2, USA). Scale bar is 1 µm (left) and 5 µm (middle). Right : Cu L_3-edge XANES for the area highlighted on the left figure, which intense white line is typical of Cu(II).

DISCUSSION

The XAFS, µ-XAFS and STXM information at the K and L_3 edges of copper in seven samples of chrysocolla suggests that this mineral is composed of mesoscopic Cu-rich domains that are similar in structure to $Cu(OH)_2$ (spertiniite). This information is consistent with infra-red spectroscopic information on chrysocolla [5], which evidenced the presence of Si-rich amorphous domains ("chalcedony"). Hence, chrysocolla appears to be a mixture of submicron- to micron-sized spertiniite-like (Cu-rich) and "chalcedony"-like (Si-rich) domains, as well as molecular water. Except minor amounts of Al, $Cu_2H_2Si_2O_5(OH)_4 \bullet nH_2O$ can then be rewritten as $2Cu(OH)_2 + 2SiO_2 + (1+n)H_2O$. The x-ray diffraction of chrysocolla must be close to that for spertiniite, which is also orthorhombic. Therefore, chrysocolla might not a compositionally homogeneous mineral as is generally assumed. Then, its validity as a unique mineral species must be reconsidered.

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REFERENCES

1. D.A. McKeown, *J. Non-Crystall. Sol.* 180, 1-10 (1994).
2. M. Winterer, *J. de Physique* IV (7-C2), 243-244 (1997).
3. S.-F. Cheah et al., *Amer. Mineral*. 85, 118-132 (2000).
4. Muñoz, M, et al., *Amer. Mineral*. 88, 694-700 (2003).
5. F.V. Chukhrov et al., *Iz. Akad. Nauk* 6, 29-44 (1968).
6. H. Funke, *Phys. Rev. B*, **71**, 094110 (2005)